about 30%. Using the kinetic scheme that assumes reaction 21 to be predominant, on the other hand, the different initial concentrations give k_5/k_{13} ratios that differ from each other by two orders of magnitude (but are still in the range 10^{-4}–10^{-6}). In other words, the variation of initial quantum yields with reactant concentrations seems to be incompatible with the reaction scheme in which reaction 21 is predominant.

It thus appears that, in contrast to systems in which oxygen interacts with polyatomic organic triplet state molecules, the oxygen–iodine triplet state interaction yields a slow rate of triplet quenching and energy transfer. Two possible causes of this slow rate can be put forward, one of them due to the diatomicity of the triplet molecules, the other due to the presence of heavy atoms.

In the first instance, one notes that there is an exothermicity of the energy transfer reaction of some 4000 cm^{-1} that must be absorbed either by the single vibrational mode of the diatomic molecules or by the solvent "sink." This represents a quite severe restriction compared to energy transfer from I_2 to naphthacene or from naphthacene to O_2, where the participation of a polyatomic molecule in the reaction provides multiple channels, in the form of a large number of vibrational modes, to accept the excess energy. Put in other words, the energy density of final states is enormously higher for the energy transfer reaction involving one polyatomic participant than for one involving two diatomic participants.

Alternatively, one could view the I_2–O_2 interaction as involving complex formation

$${}^3I_2 + {}^3O_2 \rightleftarrows {}^5(I_2\cdot O_2) \qquad (22a)$$

$$\rightleftarrows {}^3(I_2\cdot O_2) \longrightarrow I_2 + {}^3O_2 \qquad (22b)$$

$$\longrightarrow {}^1(I_2\cdot O_2) \longrightarrow I_2 + {}^1O_2 \qquad (22c)$$

with the singlet, triplet, and quintet states of the complex all being excited electronic states. In this case, the intersystem crossing reaction

$${}^1(I_2\cdot O_2) \longrightarrow {}^3(I_2\cdot O_2) \qquad (23)$$

would be heavy-atom enhanced to a great degree and, being an intersystem crossing from excited singlet to triplet, could be extremely rapid provided that the tetratomic complex could be likened to a polyatomic system where such intersystem crossing competes favorably with fluorescence. The low rate of singlet oxygen formation would then be due to the competitiveness of reaction 23 with 22c. Whether or not excimer complexes between iodine and oxygen exist is an open question. We have observed apparent inhibition of oxygen-induced fluorescence quenching when iodine is added to a fluorescent solution, which may be taken as evidence for iodine–oxygen complex formation and thus lends some support to the complexation hypothesis. The evidence, however, is not at all conclusive.

In the iodine-sensitized photooxidation of naphthacene, as a result of the large differences between energy transfer efficiencies, virtually all of the photooxidation is effected by iodine–naphthacene–oxygen energy transfer. In the iodine-sensitized photooxidation of 1,3-diphenylisobenzofuran, on the other hand, the only energetically allowed transfer path is the direct iodine–oxygen transfer step. For this system, despite the high efficiency of the DPIBF oxidation step, low quantum yields have been found because of the low efficiency of the energy transfer process.

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Quenching of Photophysically Formed Singlet (${}^1\Delta_g$) Oxygen in Solution by Amines[1]

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Abstract: The quenching by amines of singlet (${}^1\Delta_g$) oxygen formed in Freon-113 solution by laser excitation within the ${}^1\Delta_g + 1v \leftarrow {}^3\Sigma_g^-$ oxygen absorption band envelope has been studied by inhibition of the oxidation of tetraphenylcyclopentadienone (tetracyclone). The quenching rate constants range from 3.1×10^4 l. mol^{-1} sec^{-1} for ethylamine to 2.1×10^6 l. mol^{-1} sec^{-1} for triethylamine and correlate with the ionization potential of the quencher.

If a solution of oxygen in Freon-113 is irradiated in the ${}^1\Delta_g + 1v \leftarrow {}^3\Sigma_g^-$ absorption band envelope with the 1.065-μm output from a Nd-YAG laser, singlet oxygen (${}^1\Delta_g$) is produced unambiguously and in quantity.[2] Other techniques for producing singlet oxygen are low-pressure microwave discharge in the gas phase and in solution by chemical means or dye photosensitization.[3] It is possible that in these other techniques extraneous chemical species may be produced and cause reactions which could be mistaken for those of singlet oxygen.

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(1) Presented at the 6th International Conference on Photochemistry, 1971.

(2) I. B. C. Matheson and John Lee, *Chem. Phys. Lett.*, 7, 475 (1970).

(3) For recent years' reviews of the generation and properties of singlet oxygen, see *Ann. N. Y. Acad. Sci.*, 171, 1 (1970).

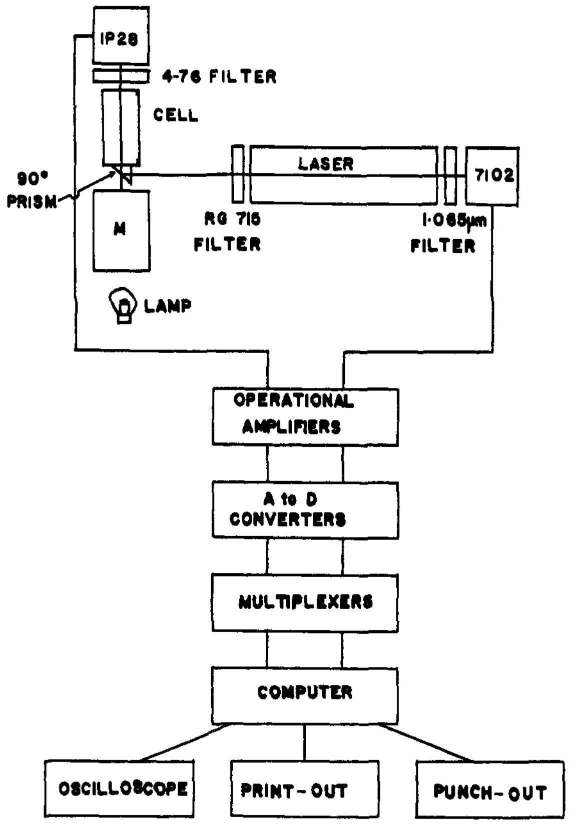

Figure 1. Schematic of apparatus for generating $O_2(^1\Delta_g)$ in a high pressure cell by absorption of 1.065-μm radiation from a Nd-YAG laser. M is a Beckmann DU monochromator for monitoring the concentration of acceptor.

Direct photophysical generation of $^1\Delta_g$ oxygen in solution has the advantage over chemical and dye sensitization methods in that the only species present are $^1\Delta_g$ and ground state oxygen. Reactions of the latter may be eliminated by blank experiments.

Ouannès and Wilson[4] have reported that aliphatic tertiary amines inhibit the reaction of $^1\Delta_g$ oxygen with known acceptors. This occurs without chemical change to the amine. Ogryzlo and Tang[5] confirmed these results and went on to show that in the gas phase the absolute quenching rate constants of a number of aliphatic amines correlated with their ionization potential.

In this present report we have studied the quenching of laser-produced $^1\Delta_g$ oxygen in Freon-113 solution under high oxygen pressure by both aliphatic and aromatic amines. In a like manner to the gas-phase results the quenching rate constants strongly correlate with the ionization potentials but their absolute values are about an order of magnitude lower than the estimates of Ogryzlo and Tang.

Experimental Section

A diagram of the apparatus is shown in Figure 1.

The reaction vessel was a high-pressure absorption cell of 50-mm path length which could withstand up to 140 atm of pressure. The cell was mounted on a modified Beckman DU single beam spectrophotometer. The 1.065-μm beam from the Nd-YAG laser (Holobeam 250 IRT) run, usually multimode C.W. at 4–6 W, was deflected into the absorption cell by means of a 7-mm right-angle prism mounted at the cell entrance. A Schott RG-715 color filter, which transmitted only above 700 nm, was placed at the laser beam entrance to prevent laser pump radiation and room light from entering the spectrophotometer cell area. The spectrophotometer RCA 1P21 photomultiplier was protected from direct laser irradiation by a Corning 4-76 color filter, which transmits only in the range 350–650 nm. The tungsten lamp of the spectrophotometer was run off a regulated dc supply to minimize lamp energy fluctuations during the course of an experiment. The laser power was monitored by a red sensitive photomultiplier (RCA 7102, S-1 response) which viewed the laser back beam through a 1.065-μm transmitting interference filter. The output of the 7102 photomultiplier was calibrated frequently relative to the laser main beam power by direct calorimetric measurement of the main beam power output. A 4% power loss at each optical surface was assumed in calculating the number of photons traversing the high-pressure cell.

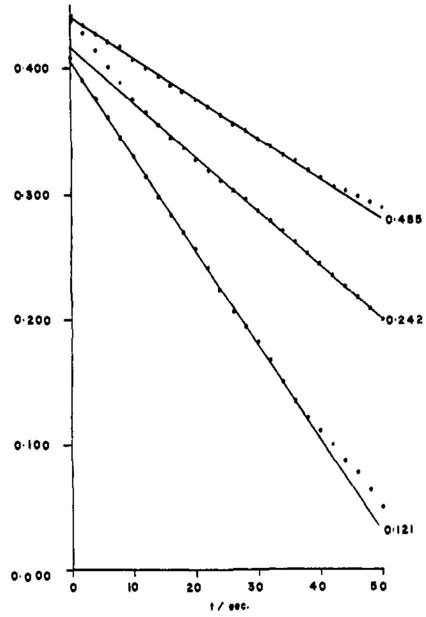

Figure 2. Decay of tetracyclone absorbance (580 nm) as a function of time caused by reaction with $O_2(^1\Delta_g)$. The concentration of ethylamine which inhibits the reaction is shown alongside each line.

The outputs of the 1P21 and 7102 photomultipliers were amplified by operational amplifiers, and the signal was then fed to analog to digital converters and then *via* a multiplexer to the Data General Nova computer. Timing was carried out relative to the internal computer clock. The outputs of both photomultipliers could be observed as a function of time on a display oscilloscope. The completion of a reaction could be observed when the photomultiplier output ceased rising with time. At this point the value for the 1P21 current was recorded, I_0, and the computer instructed to calculate the logarithm of the tetracyclone absorbance, log [log (I_0/I)], as a function of time. Upon completion of the calculations the results in the form of time, log [log (I_0/I)] and relative laser power (as measured by the 7102 photomultiplier) were either printed out or punched out on paper tape. The individual results were then corrected for laser power fluctuations and an average first-order rate constant was calculated.

Oxygen was added to the solution by applying full cylinder pressure of about 2000 psi. The oxygen concentration was determined at the end of the experiment by measuring the absorbance of the solution at 1.26 μm. Data connecting this absorbance to concentration have been previously determined.[6]

Results

The singlet Δ oxygen acceptor used for all experiments was tetracyclone,[7] K & K Laboratories, Inc., maximum initial concentration 10^{-4} *M*. Its rate of decay was measured spectrophotometrically at 580 nm. Figure 2 shows the effect of ethylamine on the absorption change

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(4) C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

(5) E. A. Ogryzlo and C. W. Tang, *ibid.*, **92**, 5034 (1970).

(6) I. B. C. Matheson and John Lee, *Chem. Phys. Lett.*, **8**, 173 (1971).

(7) T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

Table I. Quenching Rate Constants for $O_2(^1\Delta_g)$ by Amines[a]

Quencher	Slope/intercept	k_Q(soln), l. mol^{-1} sec^{-1}	k_Q(gas), l. mol^{-1} sec^{-1} [b]	Ionization potential, eV[c]
Ethylamine	$2.4 \pm 0.5 \times 10^1$	$3.1 \pm 0.6 \times 10^4$	$3.3 \pm 0.3 \times 10^5$	9.19
Diethylamine	$4.4 \pm 0.7 \times 10^2$	$5.7 \pm 0.9 \times 10^5$	$2.0 \pm 0.2 \times 10^6$	8.44
Triethylamine	$1.6 \pm 0.3 \times 10^3$	$2.1 \pm 0.3 \times 10^6$	$1.9 \pm 0.2 \times 10^7$	7.85
N-Methylaniline	$2.9 \pm 0.2 \times 10^1$	$3.8 \pm 0.3 \times 10^4$		7.84
N,N-Dimethylaniline	$1.6 \pm 0.3 \times 10^2$	$2.0 \pm 0.4 \times 10^5$		7.14

[a] All results were at 23°. [b] From ref 5. [c] From ref 8.

which under the conditions of the experiment has a pseudo-first-order decay constant.

Laser irradiation of oxygen generates $O_2(^1\Delta_g)$ in a bimolecular process[6]

$$O_2 + O_2 \xrightarrow[\sigma E]{1.065\ \mu\text{m}} O_2(^1\Delta_g) + O_2$$

where E is the laser intensity ($h\nu$, sec^{-1}) and σ the absorption cross section at 1.065 μm.

There are three loss processes given by the reactions

$$O_2(^1\Delta_g) + A \xrightarrow{k_A} AO_2$$

$$O_2(^1\Delta_g) + O_2 \xrightarrow{k_{O_2}} O_2 + O_2$$

$$O_2(^1\Delta_g) + Q \xrightarrow{k_Q} O_2 + Q$$

The first is chemical reaction with the acceptor A (tetracyclone), the second quenching by ground state oxygen, and the last quenching by the added quencher, Q.

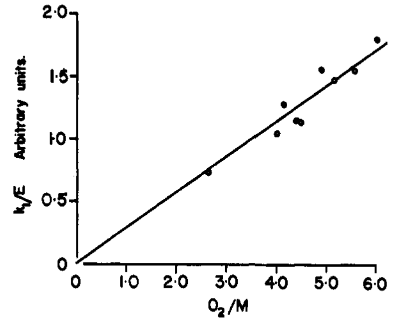

Figure 3. Variation of the tetracycline–$O_2(^1\Delta_g)$ reaction rate with oxygen concentration.

Applying the stationary state assumption for the concentration of singlet Δ oxygen, $[O_2(^1\Delta_g)]$

$$\frac{d}{dt}[O_2(^1\Delta_g)] = \sigma E[O_2]^2 - k_A[A][O_2(^1\Delta_g)] - k_{O_2}[O_2][O_2(^1\Delta_g)] - k_Q[Q][O_2(^1\Delta_g)] = 0$$

$$[O_2(^1\Delta_g)] = \frac{\sigma E[O_2]^2}{k_A[A] + k_{O_2}[O_2] + k_Q[Q]} = \frac{\sigma E[O_2]^2}{k_{O_2}[O_2] + k_Q[Q]}$$

since $k_A[A] \ll k_{O_2}[O_2] + k_Q Q$ (see ref 2).

The rate of change of acceptor concentration is

$$d[A]/dt = k_A[A][O_2(^1\Delta_g)]$$

so that the pseudo-first-order decay constant for the disappearance of 580-nm absorption is

$$k_1 = k_A[O_2(^1\Delta_g)] = \frac{\sigma E[O_2]^2 k_A}{k_{O_2}[O_2] + k_Q[Q]}$$

This may be rearranged to give

$$\frac{E}{k_1}[O_2] = \frac{k_{O_2}}{\sigma k_A} + \frac{k_Q}{\sigma k_A}\frac{[Q]}{[O_2]} \qquad (1)$$

Equation 1, on elimination of the term in [Q], may be rearranged to give

$$k_1/E = (\sigma k_A/k_{O_2})[O_2] \qquad (2)$$

This suggests that in the absence of added quenchers k_1/E should be a linear function of $[O_2]$. Such a plot is shown in Figure 3. Plots corresponding to eq 1 are shown in Figure 4.

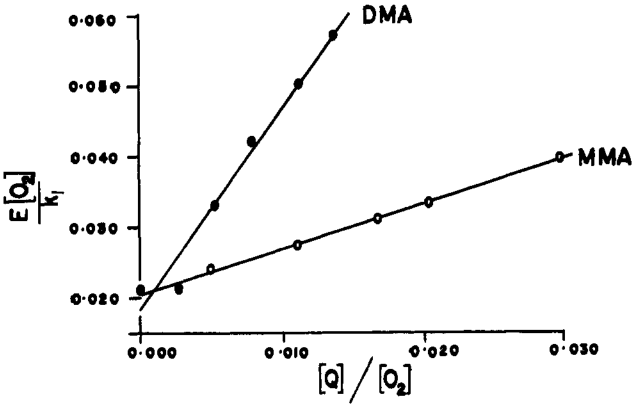

Figure 4. Quenching of the tetracyclone–$O_2(^1\Delta_g)$ reaction by *N,N*-dimethylaniline and *N*-methylaniline.

It will be noted that the ratio of slope to intercept for these plots gives k_Q/k_{O_2}. These ratios for all the amines studied are given in the first column of Table I. The second column lists the absolute value of the quenching constant obtained by multiplying the ratio by k_{O_2}. The gas-phase k_Q obtained by Ogryzlo and Tang are also listed for comparison.

Discussion

The physical quenching rates for $O_2(^1\Delta_g)$ in solution for quenchers such as these amines span about the same range as the chemical quenchers.[2] The highest rate belongs to a physical quencher, β-carotene,[9,10] but of

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(8) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold, London, 1966.

(9) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6223 (1968).

(10) I. B. C. Matheson and John Lee, *Bull. Amer. Phys. Soc.*, **17**, 327 (1972).

these amines the fastest is about 10^4 times less than the diffusion-controlled rate, roughly paralleling the gas-phase case where the fastest is 10^4 times less than the bimolecular collision frequency.

The estimated values of the solution phase quenching rate constants k_Q in Table I are approximately an order of magnitude lower than the gas phase ones. These k_Q(soln) values were calculated using the low-pressure gas-phase value for k_{O_2} of 1.3×10^3 l. mol^{-1} sec^{-1}.[11,12] Although there seems no reason to doubt the extrapolation of this value to high pressure, this rate has not so far been amenable to direct measurement in our apparatus. Attempts to measure oxygen emission from either single molecule or dimol states for both solution or gas-phase oxygen at high pressure have been unsuccessful. The experiments were done using multimode short cavity operation of the laser at up to 30 W and with a photomultiplier detection system capable of measuring a dimol (633 nm) emission rate of 10^6 photons sec^{-1}, about one-hundred times less than predicted rate of emission. This suggests the values for the radiative and quenching rate constants obtained from low-pressure gas may not be applicable at high pressure where third body effects may predominate.

Figure 5 shows the strong correlation between log k_Q(soln) and the quencher ionization potential. This relationship supports the suggestion[4,5] of a charge-transfer quenching mechanism. The aliphatic and aromatic amines, however, lie on different lines. This would be expected if the quenching mechanism involves a charge-transfer interaction since the aliphatic and aromatic amines belong to chemically different classes of electron donors.

In order to gain additional support for this mechanism, we have studied the formation of charge-transfers complexes between some of these quenchers and ground state oxygen in Freon-113.[13] These were visible as an increase in the long wavelength absorption of the donors. They were, however, of dominant stoichiometry QO_4 and weak with termolecular association constants of 0.5–3 l.^{2} mol^{-2}. As such they seem to be largely collisional. This situation does not exclude the possibility of complexes of stoichiometry $QO_2(^1\Delta_g)$, since termolecular collisions appear to be excluded by the high values of the gas-phase quenching constants. The temperature dependence of k_Q(gas) indicates that the quenching complexes must be weak and largely collisional.[5]

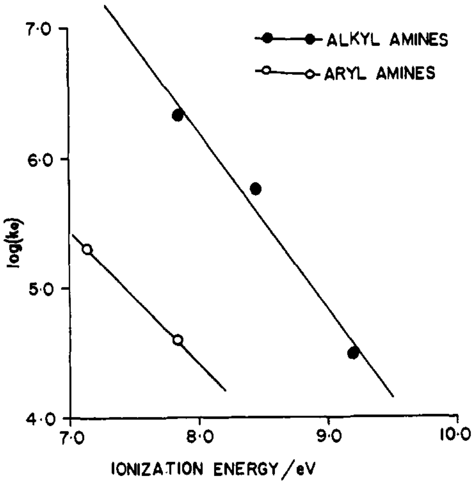

Figure 5. Relation between the quenching constant k_Q(soln) and the amine ionization potential.

In conclusion, the dependence of the quenching rate of amines for $O_2(^1\Delta_g)$ on the ionization potential of the amine and its electron donor class adds support to the charge-transfer quenching mechanism. The difference in absolute magnitude of the quenching rates between the low-pressure gas and high-pressure liquid condition may be the result of an unexpected enhancement of the rate of quenching by ground state oxygen at high pressure or may represent a true enhancement of the amine quenching rates on going into solution. The details of these mechanisms, however, remain obscure.[14]

Acknowledgments. We thank John E. Wampler for assistance with the computer programming. This research was supported in part by grants from the Research Corporation and the National Science Foundation, GP-24008.

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(11) R. P. Wayne, *Advan. Photochem.*, 7, 311 (1969).

(12) K. H. Becker, W. Groth, and U. Schurath, *Chem. Phys. Lett.*, 8, 259 (1971).

(13) I. B. C. Matheson and J. Lee, unpublished results.

(14) NOTE ADDED IN PROOF. Traces of atomic oxygen apparently led to the higher values of the singlet oxygen amine quenching constants in the gas phase reported in ref 5. A revised value of k_Q(gas) is 2.0×10^6 l. mol^{-1} sec^{-1} for triethylamine [K. Furukawa and E. A. Ogryzlo, *Chem. Phys. Lett.*, 12, 370 (1971)] in good agreement with the k_Q(soln) in Table I above.